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Temperature Dependent Surface Tension in Polymer Thin Film

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Beamline(s): X22C

Introduction: We have performed temperature dependent x-ray diffuse scattering measurements of Polystyrene (Molecular weight 891,000) thin film of thickness ~300Å. The thickness is close to the radius of gyration and the films are deposited on hydrophilic Silicon (100) substrates by spin coating technique. X-ray diffuse scattering measurements were performed in beam line X22C of the National Synchrotron Light Source (NSLS).

The in-plane correlation of a thin polymer film can be described using capillary wave theory [1]. It is known that the displacement-displacement correlation function in this theory can be written as [1,2] $C(R) = (k_BT/2\pi\gamma)\, K_0(\kappa R)$ where $K_0(\kappa R)$ is the modified Bessel function. If we use the approximation that $K_0(\kappa R)$ has logarithmic dependence then the observed diffuse scattering intensity can be modeled with Kummer functions [1]. From Kummer function fits, we can determine the slope of the asymptotic diffuse scattering tail $q_x^{\eta-1}$ with the exponent $\eta=k_BTq_z^2/2\pi\gamma$ and also the branching point from the gaussian shaped specular peak. The exponent in the power law regions and the ratios of observed intensities between the “central” and “tail” regions are determined by temperature (T) and surface tension (γ) of the polymer film. In Fig 1, log-log plots of scattered intensity vs. q_x are shown for three q_z values of 0.22Å^{-1}, 0.26Å^{-1} and 0.33Å^{-1}, each at temperatures 60ºC, 120ºC and 150ºC. We notice that the “tail” region of the data is having a single slope and there is no signature of any hump as observed earlier [2]. The q_z dependence of η in the power law region is the fingerprint of a logarithmically diverging correlation function. The temperature dependence [3] of surface tension of polymer in this temperature range can be written as $\gamma = \gamma_0\,(1 - T/T_C)^{\mu}$ where γ_0 is the surface tension at 0K temperature, μ~11/9 and the critical temperature $T_C \cong$ 1000K. This variation of γ in turn gives rise to quadratic temperature dependence of η and σ^2, where σ is the roughness. We have already observed quadratic temperature dependence in σ^2 in energy dispersive reflectivity measurements of polymer films [4]. Systematic data analysis of the transverse diffuse data (shown in Fig 1) will enable us to understand the role of capillary wave in the spinodal dewetting mechanisms of thin polymer films [5].

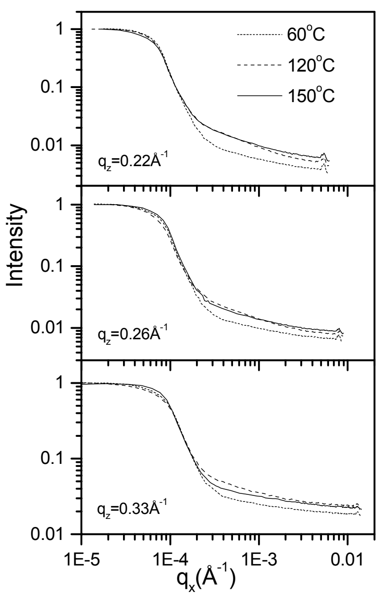

Fig 1 Log-log plot of the transverse diffuse data.

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